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(54) **Method for improving thickeners for aqueous systems.**

(57) A method is provided for improving thickeners used in aqueous system. The method involves the reversible complexation of cyclodextrin compounds with hydrophobic moieties on the thickener molecule to suppress the viscosity of the aqueous solution containing the thickener so that such the solution can be easily handled. This complexation step may be followed by decomplexing the cyclodextrin from the thickener to permit the thickener to perform its intended function.

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The present invention is concerned with a method for improving thickeners used in aqueous systems, such as, for example, aqueous latex paint formulations. In particular, the present invention is concerned with improving certain hydrophobic thickeners used in aqueous solutions which require the presence of organic co-solvents. More particularly, the invention is concerned with the use of cyclodextrin compounds for reversibly complexing with hydrophobic moieties on the thickener, resulting in the suppression of the viscosity of aqueous solutions containing such thickeners.

Aqueous systems, such as for example coatings containing emulsion polymer binders, typically employ thickeners to obtain the desired degree of viscosity needed for the proper formulation and application of the aqueous system. One general type of thickener used in aqueous systems is referred to in the art by the term "associative". Associative thickeners are so called because the mechanism by which they thicken is believed to involve hydrophobic associations between the hydrophobic species in the thickener molecules themselves and/or with other hydrophobic surfaces. A number of different types of associative thickeners are known. Typical associative thickeners include, polyurethanes, hydrophobically modified alkali soluble emulsions, hydrophobically modified hydroxyethyl cellulose or other natural products, and hydrophobically modified polyacrylamides.

Some associative thickeners, such as for example the polyurethane thickeners, are sold as aqueous solutions containing organic co-solvents. The function of the organic co-solvent, such as for example propylene glycol, is to suppress the viscosity of the aqueous solution containing the associative thickener to allow for ease in its handling before its use as a thickener.

Viscosity suppression may also be accomplished by the use of surfactants.

There are many references which disclose various hydrophobic compounds which act as associative thickeners. The associative thickeners are formulated with organic co-solvents or surfactants for use in thickening aqueous latex systems.

For example, US-A-4,155,892 and US-A-4,079,028 disclose polyurethane thickeners, characterized by at least three hydrophobic groups interconnected by hydrophilic polyether groups, formulated with organic co-solvents.

US-A-4,426,485 discloses a water-soluble thermoplastic, organic polymer having an average molecular weight of at least about 10,000 comprising hydrophobic segments each containing at least one monovalent hydrophobic group covalently bonded to the polymer, wherein the polymer has an amount of hydrophobic "bunching" comprising at least two monovalent hydrophobic groups per hydrophobic segment, sufficient to provide for enhanced thickening of aqueous solutions containing the polymer.

US-A-4,496,708 discloses to water-soluble polyurethane comb polymer thickeners.

US-A-4,499,233 discloses polyurethane thickeners in solution form in a water compatible solvent.

US-A-4,180,491 discloses urethane associative thickeners which use a non-aqueous, inert organic diluent.

Japanese Patent Disclosure No. 60-49022 describes using ethanol or surfactants with water for the dissolution of urethane associative thickeners.

None of the afore-mentioned references, however, discloses or suggests a suitable method for providing the thickener in an aqueous solution at a handleable viscosity without the use of organic co-solvents or surfactant alone.

While organic co-solvents perform their intended function, they possess potential environmental, safety and health disadvantages.

While surfactants present no specific health/ environmental hazard, they do degrade formulation performance.

It would therefore be advantageous if one could develop more environmentally acceptable and safe materials which could be used in place of organic co-solvents or just surfactants alone.

It is therefore an object of the present invention to provide a method for improving associative thickeners by eliminating the need for organic co-solvents or surfactants alone.

According to a first aspect of the present invention there is provided an aqueous system comprising a hydrophobic thickener characterised in that the aqueous system further comprises a cyclodextrin.

The term cyclodextrin includes at least one modified cyclodextrin and / or at least one unmodified cyclodextrin.

According to a second aspect of the present invention there is provided a thickener for preparing an aqueous system, the thickener comprising a cyclodextrin complexed with a hydrophobic thickener.

According to a third aspect of the present invention there is provided the use of a cyclodextrin for the preparation of an aqueous system comprising a hydrophobic thickener.

According to a fourth aspect of the present invention there is provided the use of a cyclodextrin in an aqueous system comprising a hydrophobic thickener for complexing with the hydrophobic thickener to reduce the viscosity of the system.

According to a fifth aspect of the present invention there is provided a process for preparing an aqueous system comprising mixing a hydrophobic thickener with a cyclodextrin, and optionally subsequently adding to the aqueous system a decomplexing agent for decomplexing or desorbing the cyclodextrin from the hydrophobic thickener.

5 According to a sixth aspect of the present invention there is provided a paint comprising a cyclodextrin. Preferred embodiments are set out in the claims.

Further aspects of the present invention include firstly, a method for eliminating the need for organic solvents for hydrophobic thickeners useful for thickening aqueous systems comprising: complexing said thickener with an effective amount of a cyclodextrin-containing compound, adding an effective amount of said complexed thickener to said aqueous system, and decomplexing said cyclodextrin-containing compound from said thickener with an effective amount of a compound having an affinity for said cyclodextrin-containing compound.

10 Secondly, a method for reversibly reducing the viscosity of an aqueous solution containing a hydrophobic thickener comprising reducing the viscosity of said aqueous solution by adding to said solution an effective amount of a cyclodextrin-containing compound and increasing the viscosity of said aqueous solution containing said cyclodextrin-containing compound by adding to said solution at least one mole, per mole of said cyclodextrin-containing compound, of a compound having an affinity for said cyclodextrin-containing compound.

15 Thirdly, a method of using a cyclodextrin-containing compound for reducing the viscosity of aqueous solutions containing hydrophobic thickeners comprising adding an effective amount of said cyclodextrin-containing compound to said aqueous solution containing said hydrophobic thickener.

20 Fourthly, a method of improving the incorporation of a hydrophobically modified associative thickener into an aqueous formulation comprising adding to said formulation an effective amount of a cyclodextrin-containing compound.

Fifthly, a method of reducing the loss of viscosity of an aqueous system containing a colourant comprising adding to said aqueous system containing said colourant an effective amount of a cyclodextrin-containing compound.

25 Sixthly, a method for improving the efficiency of associative thickeners in aqueous system comprising adding to said system an effective amount of a cyclodextrin-containing compound.

Seventhly, a method for reducing the colour development problems associated with surfactants in aqueous paint formulations comprising adding an effective amount of a cyclodextrin-containing compound to said paint formulation.

30 Eighthly, a method for reducing foaming in a latex paint comprising adding an effective amount of a cyclodextrin-containing compound to said latex paint.

35 Preferably, the cyclodextrin-containing compound is selected from the group consisting of alpha, beta and gamma-cyclodextrin and ethoxylated and propoxylated cyclodextrins there is provided a paint comprising a cyclodextrin.

Preferably, the compound having an affinity for said cyclodextrin-containing compound is an anionic, nonionic or cationic surfactant there is provided a thickener for an aqueous system comprising a cyclodextrin complexed with a hydrophobic thickener.

40 Preferably, the surfactant is added to said aqueous system at a concentration of about one mole per mole of said cyclodextrin-containing compound the use of a cyclodextrin for the preparation of an aqueous system comprising a hydrophobic thickener.

Preferably, the hydrophobic thickener is selected from the group consisting of hydrophobically modified polyethoxylated urethanes, hydrophobically modified alkali soluble emulsions, hydrophobically modified hydroxyethyl cellulose or other natural products, and hydrophobically modified polyacrylamides.

45 Preferably, the effective amount of said cyclodextrin-containing compound used to complex with said thickener reduces the viscosity of the thickener to a handleable viscosity but is not greater than the water solubility of said cyclodextrin-containing compound.

The present invention therefore provides a method for improving associative thickeners by the addition of at least one cyclodextrin compound to aqueous solutions containing associative thickeners. The cyclodextrin compound suppresses the viscosity of aqueous solutions containing associative thickeners and eliminates the need for organic co-solvents. In addition, the viscosity suppressing function of the cyclodextrin compound is readily reversed, as needed, by the addition of a compound having an affinity for the cyclodextrin, such as for example a surfactant, thereby providing an effective associative thickener for aqueous systems.

50 In other embodiments of the invention, the cyclodextrins have been found to improve the ease of incorporating hydrophobically modified, associative thickeners, having marginal solubility in water, into aqueous systems; to reduce the viscosity drop of associative thickener containing formulations upon the addition of colourants or surfactants to the formulation; to improve the efficiency of the associative thickener itself, thus reducing the amount of thickener required to reach a given paint viscosity; to reduce foaming in a latex paint;

and to reduce the colour development problems caused by surfactants in some formulations.

It is known that cyclodextrin compounds are cyclically closed oligosaccharides with 6, 7 or 8 alpha-D-glucoses per macrocycle. The six glucose ring cyclodextrin compound is referred to as an alpha-cyclodextrin; the 7 glucose ring cyclodextrin compound is referred to as a beta-cyclodextrin; and the 8 glucose ring cyclodextrin compound is referred to as the gamma-cyclodextrin. Cyclodextrins are produced from starch of any selected plant variety, such as corn, potato, waxy maize, and the like which may be modified or unmodified starch derived from cereal or tuber origin and the amylose or amylopectin fractions thereof. The selected starch in the form of an aqueous slurry, at concentrations up to about 35 % by weight solids, is usually liquefied, for example by gelatination or treatment with a liquefying enzyme such as bacterial alpha-amylase enzyme, and then subjected to treatment with a transglycosylase enzyme to form the cyclodextrins. The amount of individual alpha-, beta- and gamma-cyclodextrins will vary depending on the selected starch, selected transglycosylase enzyme and processing conditions. Precipitation and separation of the individual cyclodextrins is described in the literature using solvent systems, inclusion compounds, such as trichloroethylene, and non-solvent systems utilizing selected ion exchange resins. Each of the cyclodextrins, as well as mixtures thereof, is a commercially available material. Beta-cyclodextrin is the most widely used form and is known for use in the production of pharmaceuticals and foods.

The ability of cyclodextrins to form inclusion complexes with organic compounds and thereby increase the water solubility of the organic compound is known. In Cyclodextrins Increase Surface Tension and Critical Micelle Concentrations of Detergent Solutions by W.Saenger and A.MullerFalmow, Agnew.Chem. Int. Ed. Engl. 27 (1988) No.3 at pages 393-394, the authors discuss the ability of the central hydrophobic cavity of the cyclodextrin compounds to accommodate the hydrophobic, aliphatic part of a detergent molecule having a diameter of about 5 Angstroms. Studies with such detergents showed that the cyclodextrins were capable of increasing the surface tension of the detergent molecule and shifting the critical micelle concentration of the detergent to a higher value, thus making the detergent more soluble in water. This was suggested as being beneficial in cases where micelles need to be destroyed or where surface tension needs to be increased, as for example to avoid foaming.

GB-A-2,189,245 entitled Producing Modified Cyclodextrins, published on Oct.21, 1987, and assigned to American Maize-Products Company discloses a method for increasing the water solubility of cyclodextrins. This method involves modification with alkylene carbonates and preferably ethylene carbonate to form hydroxyethyl ethers on the ring structure.

The applicants have found that cyclodextrin compounds can be absorbed onto the hydrophobic moieties of associative thickeners because they can absorb onto or form complexes with hydrophobic species. The absorption of cyclodextrin compounds onto the hydrophobic moieties of associative thickeners causes a suppression of the viscosity of an aqueous solution containing the associative thickener. It has been found that cyclodextrin compounds can be readily desorbed or decomplexed from the associative thickener by the addition of another material which has an affinity for the cyclodextrin.

The applicants have found that not only can the alpha-, beta- and gamma-cyclodextrins be used effectively as transient viscosity suppressing agents for hydrophobic associative thickeners, but that modified cyclodextrins, such as for example those cyclodextrins produced by the process described in GB-A-2,189,245, which are more soluble in water than the unmodified cyclodextrin compounds can also be employed in this manner. In fact, the applicants have found it preferable to utilize hydroxyethyl- or hydroxypropyl-cyclodextrins having a higher degree of water solubility than the unmodified cyclodextrins for use with aqueous solutions containing high concentrations of associative thickener.

The least water soluble of the unmodified cyclodextrins is beta-cyclodextrin. The water solubility limit of beta-cyclodextrin is about 2 grams per 100 grams of water. This limits the concentration of beta-cyclodextrin which can be employed to suppress the viscosity of an aqueous solution containing an associative thickener. Since the viscosity of an aqueous solution containing an associative thickener increases with the concentration of the associative thickener solids, the solubility limit of the cyclodextrin determines the maximum amount of cyclodextrin which can be added to the solution without resulting in the formation of undesirable solids. If the maximum concentration of a viscosity suppressing additive needed to reduce the viscosity of an aqueous solution containing an associative thickener to a handleable viscosity, such as for example a viscosity of about 2,000 cps, exceeds the solubility limit of the additive in water, then the additive is not effective as a viscosity suppressant additive. In other words, the effectiveness of a cyclodextrin as a viscosity suppressing additive is a function of the solubility limit of the cyclodextrin and the solids content of the associative thickener in the aqueous solution. The higher the solids content of the associative thickener the higher the viscosity of the aqueous solution containing it will be and, likewise, the higher the concentration of the cyclodextrin which will be needed to be added to suppress the viscosity down to a handleable viscosity. This relationship between the solubility limit of the cyclodextrin and the viscosity of an aqueous solution containing an associative thick-

ener is critical in the selection of an effective cyclodextrin for use as a viscosity suppressing additive. As described in more detail below, this relationship favors the selection of unmodified cyclodextrins other than beta-cyclodextrin, and modified cyclodextrin additives having increased water solubility in cases where the aqueous solutions contains high concentrations of associative thickener solids.

5 The applicants have found that the use of beta-cyclodextrin and its ethoxylate and propoxylate derivatives are useful in latex paint formulation for achieving a variety of effects, such as for example: to permit the preparation and supply of a low viscosity, high solids solution of the thickener without the use of viscosity suppressing solvent; improving the ease of incorporating hydrophobically modified, associative thickeners, having marginal solubility in water, into aqueous systems; to reduce the viscosity drop of associative thickener containing formulations upon the addition of colourants or surfactants to the formulation; to improve the efficiency of the associative thickener itself, thus reducing the thickener required to reach a given paint viscosity; to reduce foaming in a paint, with or without an associative thickener, which is especially desirable when the paint is to be applied by a roller; and to reduce the colour development problems caused by surfactants in some formulations.

15 In aqueous solutions containing low concentrations of associative thickener solids, for example on the order of about 3 percent by weight, the applicants have found that the unmodified cyclodextrins, including beta-cyclodextrin, are effective viscosity suppressing additives, while in aqueous solutions containing high concentrations of associative thickener solids, for example on the order of greater than about 10 percent by weight, modified cyclodextrins, having increased water solubility on the order of about 50 grams per 100 grams water, are preferred.

20 As illustrated in the Examples which follow, the applicants have found that handleable viscosities can be achieved with polyurethane type associative thickeners at low solids concentrations from about 3% to 12 % by weight using from about 0.5 % to 2 % of a beta-cyclodextrin having a water solubility of 2 grams per 100 grams water. Modified cyclodextrins, such as for example the hydroxyethyl- or hydroxypropyl- cyclodextrins, can also be effectively used with low solids associative thickeners. With high solids associative thickeners containing approximately 20% by weight of a urethane associative thickener, the applicants found that only the modified cyclodextrins were effective viscosity suppressing additives since the concentrations which were required to be added exceeded the water solubility limits of the unmodified cyclodextrins. In the case of such high solids urethane associative thickeners we found that it was necessary to employ about 10% of the modified cyclodextrins to achieve handleable viscosities.

30 The ability to decomplex the cyclodextrin additive from the hydrophobic associative thickener is just as important as the ability of the cyclodextrin to absorb or complex with the associative thickener in the first instance. It is critical that the cyclodextrin becomes decomplexed or desorbed from the hydrophobic moieties on the associative thickener molecule in order to enable the thickener to perform its intended viscosity increasing function in the aqueous system to which the associative thickener solution is added.

35 The applicants have found that cyclodextrins are readily desorbed or decomplexed from hydrophobic associative thickeners simply by the addition of a material which has an affinity for the cyclodextrin. In this regard the applicants have found that conventional surface active agents commonly employed in aqueous coating systems, such as for example anionic surfactants like sodium lauryl sulfate and non-ionic surfactants such as for example Igepal CO-660 (Igepal CO-660, which is a trademark of Dorset Inc, is a 10 mole ethoxylate of nonyl phenol) and cationic surfactants, may be used to decomplex or desorb the cyclodextrin. Other water soluble organic solvents, such as for example ethanol and Texanol (2,2,4-trimethyl-3-hydroxypentyl acetate), may also be employed for this purpose.

45 The applicants have found that it is preferable to utilize about one mole of the decomplexing agent per mole of the cyclodextrin added to the associative thickener solution in order to achieve complete desorption or decomplexation. Both the complexation and decomplexation mechanisms are easily achieved by the addition of the reactants with mixing. No special purification or separation steps are required.

50 In experiments with certain latex paint formulations the applicants unexpectedly found that it is not necessary to add additional surfactant to cause the decomplexation process to occur; the formulation surfactants already present in the paint were found to be sufficient. When the cyclodextrin-modified thickeners are added to the paint formulation at equal levels, based on the thickener component in the formulation, those modified with cyclodextrin have been shown to possess a slightly better efficiency (higher equilibrated Krebs-Stormer viscosity) than those containing the unmodified thickener. Formulation surfactants in the paint tend to suppress the development of associative thickening. Therefore, the formation of the surfactant-cyclodextrin complex, which occurs as the thickener is activated, reduces the effective surfactant concentration in the formulation, thus increasing the equilibrated viscosity. Addition of further surfactants over a wide range of hydrophilic-hydrophobic balances (HLBs) and from 1 to 5 mole equivalents of surfactant to cyclodextrin causes a decrease in viscosity. Those thickeners modified with cyclodextrins, especially the propoxylate modified cyclodextrins, are

less affected by the surfactant addition.

The viscosity stabilizing effect of the cyclodextrins can be further utilized by post adding the cyclodextrins to the associatively thickened formulation. As demonstrated by illustrative Example 9 presented hereinafter, the viscosity loss which occurred upon the addition of predispersed colourant to the formulation was reduced by increasing levels of cyclodextrins. The data presented in Example 9, clearly demonstrate the innate viscosity instability of this type of associative thickener can be reduced by the post-addition of cyclodextrins thus making the thickener less formulation sensitive.

One of the limitations in associative thickener chemistry is the latitude one has on the size of the hydrophobe relative to the hydrophilic backbone of the molecule. As the hydrophobe become larger, it becomes more associative and thus more efficient. However, a practical limitation is reached when the thickener can no longer be incorporated into the aqueous phase of the paint. In current associative thickener technology, the incorporation of the thickener in many formulations is undesirably slow. The applicants have demonstrated that the speed of incorporation of the thickener can be improved, as will be illustrated by the examples presented hereinafter, by the incorporation of cyclodextrin. To do this, cyclodextrin modified and unmodified thickener were added to separate formulations and the time required for the thickener to dissolve in each of the formulation was measured under similar stirring conditions for each of the thickeners. The results demonstrated that cyclodextrins modified thickeners were incorporated in one fourth of the time required by the unmodified thickener.

The surfactant complexing effect of the cyclodextrins are also of benefit to the formulator for other properties than rheological modification.

For example, typically, when formulating tinted paints, the composition of the formulation, specifically the surfactants, must be modified to maintain the stability of the colourant dispersion while not adversely affecting the dispersion of the other components. In some formulations, the paint components, such as the latex vehicle, bring an incompatible surfactant into the formulation. To correct for this, additional surfactants are added to the formulation to compatibilize the system. While effective in compatibilizing the system, these surfactants can contribute adverse water sensitivity and foaming characteristics to the formulation. In the illustrative examples, presented hereinafter, we have demonstrated that cyclodextrins are useful in improving the compatibility of a colourant without the need for adding additional surfactants.

The surfactant complexing effect of the cyclodextrins is also of benefit to the formulator for other properties. For example, foaming in the formulated paint must be combatted, because of the high surfactant loading required to prepare many latex paint vehicles. Current technologies for foam reduction are limited in efficacy by the formulation and application problems that they can cause. In using a cyclodextrin, which may or may not be modified, such as for example ethoxylated cyclodextrins, the foaming tendency of the formulations is reduced without the development of any adverse phenomena such as surface defects.

The present invention will now be described by way of examples only.

Example 1: Low Solids

This Example demonstrates the effectiveness of beta-cyclodextrin to suppress the viscosity of an aqueous solution of a polyurethane associative thickener (Rohm and Haas Company, QR-708) at a low solids content of 3% by weight (3 grams solid QR-708 in 97 grams water). The associative thickener aqueous solution was prepared as follows: differing quantities of beta-cyclodextrin (American Maize Company) were added to aliquots of the associative thickener solution (3g solid QR-708 in 97g H₂O) with mixing in a jar on a shaker for 4 hours and allowed to stand overnight. The viscosity of each of the solutions was measured using a Brookfield viscometer (spindle number 4) at 30 rpm. Table 1 shows the results of the addition of the beta-cyclodextrin to the associative thickener solutions.

Table 1

	Sample	beta-cyclodextrin (grams)	viscosity (cps)
5	1	0	210
	2	0.0009	210
10	3	0.0117	192
	4	0.0512	196
	5	0.1010	204
15	6	0.1996	177
	7	0.3030	108
	8	0.4016	35
20	9	0.5056	14
	10	1.0077	7

25 The results show that the viscosity of the associative thickener solution steadily falls as the amount of cyclodextrin is increased.

Example 2: Restoration of viscosity: anionic and nonionic surfactants

30 Next the applicants determined whether it was possible to restore the viscosity of aqueous solutions containing 3% QR-708 (3 grams solid QR-708 in 97 grams water) and 1 gram beta-cyclodextrin to the original viscosity level of the 3% QR-708 solution by adding sodium lauryl sulfate ("SLS", 28%). In order to determine this, the applicants measured the viscosity of the solution as in Example 1 as the amount of SLS was added. Table 2 shows the results.

Table 2

	Sample	SLS (grams)	viscosity (cps)
40	11	0.01	10
	12	0.09	10
	13	0.47	48
45	14	0.89	191

The results demonstrate that the original viscosity of the solution is recovered upon the addition of 0.25 grams of SLS solids (0.89 grams of 28% SLS), which is equivalent to 1 mole of SLS per mole of beta-cyclodextrin added.

50 This experiment was repeated using a nonionic surfactant, Igepal CO-660. The results are shown in Table 3.

Table 3

	Sample	Igepal CO-660 (grams)	viscosity (cps)
5	15	.29	50
	16	.58	725

These results show that the original viscosity is recovered upon the addition of 0.58 grams of the nonionic surfactant, which is equivalent to 1 mole per mole of beta-cyclodextrin.

EXAMPLE 3: Restoration of viscosity: cationic surfactants and organic solvents

The following quantities of a cationic surfactant 18/25 (which represents Ethoquad which is the registered trade mark of Akzo Chemicals Inc. and is chemically methylpolyoxyethylene (15)octadecyl ammonium chloride) were added to a solution of 3g of a 100% solids QR-708 (3 grams solid QR-708 in 97 grams water) and 1g of beta-cyclodextrin (from American Maize) in 97g of deionized (DI) water. Table 4 shows the results.

Table 4

	Sample	Cationic Surfactant 18/25	viscosity, cps	Spindle #
25	17 Comparative	0g	5	1
	18	.23g	11	1
	19	.45g	123	1
30	20	.68g	484	3
	21	.91g	1,060	4

Viscosities were determined on a Brookfield viscometer at 30 rpm using the spindle number indicated above.

The results show shows that the original visosity is recovered upon the addition of 0.91g. of the cationic surfactant.

Further, the ability of organic solvent for recovering original viscosity was also examined using Texanol (2,2,4- trimethyl-3-hydroxypentyl acetate, Texanol is a trademark of Texaco) and propylene glycol. The results are shown in Table 5.

Table 5

	Sample	Texanol, grams	Propylene glycol, grams	viscosity, cps
45	22	0.10	--	18
	23	0.19	--	299
50	24	--	.03	7
	25	--	0.07	6
	26	--	0.14	6
55	27	--	0.21	8

The results show that, in this particular example, the organic solvents are less effective than either of the surfactants for recovering original viscosity, and while Texanol was useful, propylene glycol was not.

Example 4: High Solids

This Example demonstrates the effectiveness of beta-cyclodextrin as a viscosity suppressing additive for high solids urethane thickener solutions. A series of samples containing either 0 grams, 1.5 grams or 2 grams beta-cyclodextrin and varying concentrations of the urethane associative thickener (total solution weight is 100g) were prepared in accordance with Example 1. Table 6 shows the viscosity of each of the solutions.

Table 6

	Sample	Beta-cyclodextrin grams	QR-708 % solids	Viscosity cps
10	28Comparative	0	3	1,180
	29 "	0	5	3,500
15	30 "	0	7.5	44,700
	31 "	0	10	154,800
	32 "	0	12.5	353,600
	33 "	0	15	454,000
20	34 "	0	17.5	665,000
	35 "	0	20	870,000
	36	1.5	3	60
	37	1.5	5	70
25	38	1.5	7.5	4,750
	39	1.5	10	4,750
	40	1.5	12.5	20,150
	41	1.5	15	40,000
	42	1.5	17.5	214,000
30	43	1.5	20	478,000
	44	2.0	3	7
	45	2.0	5	12
	46	2.0	7.5	35
35	47	2.0	10	1,050
	48	2.0	12.5	15,650
	49	2.0	15	27,800
	50	2.0	17.5	86,900
40	51	2.0	20	240,800

The results show that a viscosity of about 2000 cps can be achieved at around 10% QR-708 solids using 2 grams of the beta-cyclodextrin, while this viscosity can be achieved at about 7% solids using 1.5 grams beta-cyclodextrin.

Example 5: Alpha- and Gamma-Cyclodextrins

This Example demonstrates the effectiveness of alpha-cyclodextrin and gamma-cyclodextrin as viscosity suppressing additives for urethane associative thickeners.

To solutions containing 3 grams QR-708 (100% solids) were added the materials shown in Tables 7 and 8 respectively. The samples were then capped and agitated for three hours and then put in a water bath at 25°C. for 16 hours. The viscosity of each sample was then measured using a Brookfield viscometer at 30 rpm using the spindle # indicated.

Table 7

Alpha-Cyclodextrin

Sample	Alpha-cyclodextrin grams	Deionized Water grams	Viscosity cps	Spindle #
52 Comparative	0	97.00	1,540	4
53	0.10	96.90	900	4
54	0.25	96.75	172	3
55	0.50	96.50	14	2
56	1.00	96.00	4	1

Table 8

Gamma-Cyclodextrin

Sample	Gamma-cyclodextrin grams	Deionized Water	Viscosity cps	Spindle #
57 Comparative	0	97.00	1,540	4
58	0.10	96.90	1,340	4
59	0.25	96.75	1,096	3
60	1.00	96.00	114	2

The results show that the viscosity of each of the associative thickener solutions steadily falls as the amount of either alpha- or gamma-cyclodextrin is increased.

Example 6: Cyclodextrin Derivatives

This Example illustrates the use of modified cyclodextrins as viscosity suppressing additives for both low solids and high solids urethane associative thickeners. The cyclodextrins used were ethoxylated (EO-CD) and propoxylated beta-cyclodextrins (PO-CD) obtained from American Maize Company. The solutions were prepared and the viscosities were determined using the procedure of Example 1 (total solution weight was 100g). The results are shown in Table 9.

Table 9

Modified Cyclodextrins

Sample	Cyclodextrin Type, grams	QR-708 %solid	Viscosity cps
61 Comparative	0 EO-CD	3	1,364
62	.1	3	1,436
63	.2	3	1,184
64	.5	3	584
65	1.0	3	6
66 Comparative	0 EO-CD	20	313,600
67	2	20	298,400
68	4	20	181,600
69	5	20	135,200
70	6	20	36,400
71	7	20	20,400
72	8	20	2,984
73	10	20	684
74	2 PO-CD	20	528,000
75	4	20	133,200
76	6	20	9,600
77	8	20	760
78	10	20	460

The results show that the viscosity of each of the associative thickener solutions steadily falls as the amount of either EO-CD or PO-CD is increased.

Example 7: OTHER ASSOCIATIVE THICKENERS

This Example demonstrates the utility of the cyclodextrin additives as viscosity suppressants for aqueous solutions containing other types of associative thickeners.

The thickeners used in this experiment were: Acrysol TT-935 (Rohm and Haas Company), which is a hydrophobically modified alkali soluble emulsion thickener, and Natrosol Plus, which is a hydrophobically modified hydroxyethyl cellulose thickener (Natrosol Plus is from Aqualon). An unmodified (non-hydrophobic) hydroxyethyl cellulose thickener (HEC) was also evaluated. Each of these thickeners were formulated separately in aqueous solutions at various concentrations and the beta-cyclodextrin additive was added as described in Example 1. The viscosities of the solutions were measured as in Example 1 and the results are shown in Table 10.

Table 10

OTHER ASSOCIATIVE THICKENERS

Sample	Beta-cyclodextrin grams	Associative thickener grams and type	Viscosity cps
79Comparative	0	2.0 solid TT-935 *	411
80	0.25	" "	146
81	0.5	" "	99
82	0.75	" "	33
83	1.0	" "	21
84Comparative	0	3 Nat. Plus **	4,240
85	0.25	" "	1,380
86	0.50	" "	400
87	0.75	" "	221
88	1.0	" "	165
89Comparative	0	3 HEC ***	3,520
90	0.25	" "	4,680
91	0.50	" "	5,120
92	0.75	" "	4,720
93	1.0	" "	4,880

* (1% solution) in .8g of 50 wt% NaOH and 197.2g H2O

** (1.5% solution) in 197g H2O

*** (1.5% solution) in 197 g H2O

The results show that beta-cyclodextrin reduces the viscosity of these two hydrophobically modified thickeners, TT-935 and Natrosol Plus, but has no effect on the viscosity for the non-hydrophobic thickener hydroxyethyl cellulose (HEC).

Example 8: Latex Paint

This Example demonstrates the use of the cyclodextrin additives in aqueous latex paint formulations containing associative thickeners. The composition of the latex paint formulation used in this Example is shown below in Table 11 and the results are shown below in Table 12, in which BCD is beta-cyclodextrin, E-BCD is ethoxylated beta-cyclodextrin and P-BCD is propoxylated betacyclodextrin and HEUR is a control and represents an unmodified thickener QR-708, which is a hydrophobically modified ethoxylated urethane rheology modifier.

Table 11

Latex Paint Formulation #1

5	Material	Kg	(Pounds)
	Propylene glycol	31.75	(70.00)
10	Tamol SG-1 dispersant(35%)	5.44	(12.00)
	Foamaster VL antifoaming agent	0.45	(1.00)
15	Water	20.41	(45.00)
	Titanium dioxide Pure-R-900	95.26	(210.00)
	China Clay	39.92	(88.00)
20	Water	52.94	(116.70)
	Texanol	5.17	(11.40)
25	AC-64 acrylic binder	171.46	(378.00)
	Foamaster VL	1.36	(3.00)
	Water	19.05	(42.00)
30	Thickener plus water	42.09	(92.80)
	PVC= 29.81, Volume solids = 34.86		

35 (Tamol SG-1, which is a trademark of Rohm and Haas, is an ammonium salt of carboxylated polyelectrolyte (35% solids) and is used as a pigment dispersant; Foamaster VL, which is a trademark of Oxy Process Chemicals, is a proprietary defoamer; and Texanol, which is a trademark of Texaco, is 2,2,4-tri-methyl-3-hydroxypentyl acetate).

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Table 12

Thickening Efficiency in Latex Paint
Surfactant Addition Effects
Thickener type

	HEUR	BCD	E-BCD	P-BCD
Control				
Thickener Demand	2.72x10 ⁻³	2.72x10 ⁻³	2.72x10 ⁻³	2.72x10 ⁻³
dry Kg/l				
(dry lbs/100 gal)	(2.27)	(2.27)	(2.27)	(2.27)
(based upon thickener component)				
Viscosity - KU equil	102	110	111	105
- ICI	0.8	0.8	0.8	0.8
<u>Surfactant Addition</u>				
Triton X-45	Viscosity change (KU)			
1 mole equiv.	- 5	- 4	- 5	- 3
2	-11	- 2	- 1	- 2
5	-17	- 6	- 7	- 3
Triton X-100	Viscosity change (KU)			
1 mole equiv.	- 9	- 6	- 4	- 6
2	-27	- 6	- 6	- 5
5	-35	-14	-13	-10
Triton X-405	Viscosity change (KU)			
1 mole equiv.	-19	-11	- 8	- 5
2	-34	-15	-12	- 2
5	-39	-32	-26	- 8

The cyclodextrin modified thickeners were added to the paint formulation at equal levels based on the thickener component in the formulation. Those modified with cyclodextrins BCD, E-BCD and P-BCD (BCD is beta-cyclodextrin, E-BCD is ethoxylate beta-cyclodextrin and P-BCD is propoxylated betacyclodextrin) demonstrate better efficiency (higher equilibrated Krebs-Storm r viscosity) than the unmodified thickener control HEUR (which is QR-708, is a hydrophobically modified ethoxylated urethane rheology modifier). Addition of the further surfactants Triton X-45 (ethoxylated octyl phenols 5 EO units), Triton X-100 (9.5 EO units) and Triton X-405 (40 EO units) over a wide range of HLBs and from 1 to 5 mole equivalents of surfactant to cyclodextrin containing formulations causes a decrease in viscosity.

Exempl 9 : Latex Paint : Post addition of cyclodextrins

This Example demonstrates that the viscosity stabilizing effect of the cyclodextrin can be further utilized by the post addition of cyclodextrins to an associatively thickened paint formulation.

5 The latex paint used in this Example had the composition shown in Table 13.

Table 13

Latex Paint Formulation #2

		Amount	
15	Material	Kg	(pounds)
	Water	48.39	(106.7)
	Tamol 731(25%) dispersant	5.22	(11.5)
20	Propylene glycol	11.34	(25.0)
	Patcote 801 (defoamer)	0.91	(2.0)
	Titanium dioxide-Pure R-900	113.4	(250.0)
25	Optiwhite (China clay)	45.36	(100.0)
	Attagel 50(Attapulgate clay)	2.27	(5.0)
30	Polymeric Binder AC-64	158.76	(350.00)
	Texanol	4.81	(10.60)
	Patcote 801	1.81	(4.00)
35	Thickener plus water	106.46	(234.70)

40 PVC= 36.8, Volume solids=35.86

(Patcote, which is a trademark of Patco Designed Chemicals, is a defoamer; and Attagel, which is a trademark of Phibro Corp., is a colloidal clay.)

45 The latex paint formulation #2 was thickened to a viscosity of 110 Krebs Units with a hydrophobically modified ethoxylated urethane rheology modifier. To the thickened paint samples was post- added an equivalent of from 0 to 4.53 Kg (0 to 10 pounds) of cyclodextrin per 3781 (100 gallons) of the paint. After this, each paint was tinted to an equivalent of 59 ml (2 fluid ounces) of predispersed lampblack colourant per 3.781 (per gallon) of paint. After stirring, the Krebs-Stormer viscosity of each paint sample was again measured. The viscosity
50 difference between the initial viscosity and the viscosity after tinting was used as a measure of stability. Table 14 presents the results of this evaluation.

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Table 14

Viscosity Stability Upon colourant Addition

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	Additive Level		
	Kg/l	(lbs / 100 gal)	Viscosity Change (KU)

	0 Kg	0 lbs beta-CD	-34
15	1.19x10 ⁻³	(1)	-27
	3.57x10 ⁻³	(3)	-12
	5.95x10 ⁻³	(5)	- 3
	8.33x10 ⁻³	(7)	+ 4
20	11.9x10 ⁻³	(10)	+ 4
	0 Kg	0 lbs beta-CD ethoxylate	-34
	1.19x10 ⁻³	(1)	-25
25	3.57x10 ⁻³	(3)	-14
	5.95x10 ⁻³	(5)	- 3
	8.33x10 ⁻³	(7)	+ 4
	11.9x10 ⁻³	(10)	+ 8
30	0 lbs beta-CD propoxylate		-34
	1.19x10 ⁻³	(1)	-25
	3.57x10 ⁻³	(3)	- 8
	5.95x10 ⁻³	(5)	+ 1
35	8.33x10 ⁻³	(7)	+ 4
	11.9x10 ⁻³	(10)	+ 5

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Example 10: Time to incorporate associative thickener

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This Example demonstrates the ability of the cyclodextrins to reduce the time required for the incorporation of associative thickeners in a latex paint formulation. The associative thickener was added to latex paint formulation #1 (see Table 11) and stirred. The time required for the thickener to dissolve in the paint was measured . The results are shown in Table 15.

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Table 15

Rate of Thickener Incorporation

Thickener	Time to incorporate (min.)
HEUR (hydrophobically modified ethoxylated urethane rheology modifier-control)	120
Beta-cyclodextrin	29
Ethoxylated-beta-cyclodextrin	27
Propoxylyted-beta-cyclodextrin	29

Example 11: Compatibility of colourant

A tint base formulation (Paint formulation #3: Table 16) was prepared with and without additional colourant stabilizing surfactants. To those paints formulated without the surfactants the applicants added an equivalent of 0 to 4.53 Kg (0 to 10 lbs) of ethoxylated cyclodextrin per 378.51 (100 gallons) of paint. After equilibration, the paints were cast on a Leneta Wb sealed white chart using a 3 mil bird applicator. The paint films were allowed to dry at 77° F and 50% relative humidity for 4 days. After drying was complete, approximately 10 grams of the same paint was cast on a 7.62 cm (3") band of each chart by brush. Brushing was continued to dryness in order to provide significant shear to the paint being applied. After an overnight dry at 77° F and 50% relative humidity, the colour acceptance of each of the paints was evaluated by measuring the difference in Y-reflectance of the brush vs. Bird cast films using a spherically integrating reflectometer. If the colourant and other components of the paints are properly dispersed, there should be no shear dependent change in the Y-reflectance of the film. While perfect colour acceptance was not achieved (see Table 17), it is clear from the data that the use of an equivalent of 2.27 Kg (5 lbs) of the ethoxylated cyclodextrins per 378.51 (100 gallons) yields an improvement equal to either or both of the surfactants listed in the formulation. While degree of colour acceptance problem in this Example may be barely significant to human perception, the trend for improvement up to the 2.27 kg (5 lbs) level was clear when so measured.

Table 16

Paint Formulation #3

5	Material	Amount	
		Kg	(pounds)
10	The following were charged to the tank:		
	Tamol 850 dispersant (30%)	4.08	(9.0)
	Water	0.91	(2.0)
15	Propylene glycol	27.22	(60.0)
	Antifoamer	0.23	(0.5)
20	The following were added with low speed mixing:		
	High gloss rutile titanium dioxide	102.1	(225.0)
	Barytes (barium sulfate)	18.14	(40.0)

25 Table 16 cont'd.

The above was then ground in a high-speed mill (Cowles 3800-4500 feet per minute) for 10-15 minutes, and was then let down with the following at low speed mixing:

30		<u>Kg</u>	<u>(Pounds)</u>
	Propylene glycol	43.32	(95.5)
35	Polymeric Binder Rhoplex AC-490(46.5%)	238.59	(526.0)
	Acrysol G-110Acrylic thickener	4.67	(10.3)
	Mineral spirits	0.45	(1.0)
40	Water	31.16	(68.7)
	Butyl Cellosolve	11.11	(24.5)
	Triton N-57 nonyl phenol ethoxylate	either 0.0	or 1.81 (4.0)
45	Triton X-207 alkylaryl polyether alcohol	either 0.0	or 1.81 (4.0)
	Tint : predispersed red iron oxide	0.3 g/l	(4 ounces/100 gallons)
	PVC= 23.3%, Volume solids= 33.0%, gloss (60 degrees)=40-50		

50 (phoplex, which is a trademark of Rohm and Haas, is a polymeric binder; and Acrysol, which is a trademark of Rohm and Haas, is a thickener.)

Table 17

colour Acceptance Modification with
beta-Cyclodextrin Ethoxylate

Added Surfactant for colour Acceptance	Ethoxylated CD Kg/l (lbs/100gal)		Y-Reflectance Difference (upon shear)
1.81 kg (4lb) Triton N-57 and 1.81 kg (4lb) Triton X-207	0	(0)	0.51
	1.19x-3	(1)	0.43
	3.57x-3	(3)	0.52
	5.95x-3	(5)	0.56
	11.9x-3	(10)	0.49
1.81 kg (4lb) Triton N-57	0	(0)	0.33
	1.19x-3	(1)	0.32
	3.57x-3	(3)	0.40
	5.95x-3	(5)	0.35
	11.9x-3	(10)	0.50
1.81 kg (4lb) Triton X-207	0	(0)	0.36
	1.19x-3	(1)	0.36
	5.95x-3	(5)	0.51
	11.9x-3	(10)	0.63
No added surfactant	0	(0)	0.49
	1.19x-3	(1)	0.42
	3.57x-3	(3)	0.36
	5.95x-3	(5)	0.32
	11.9x-3	(10)	0.58

Example 12: Reduction in Foaming in Latex Paint

This Example demonstrates the use of cyclodextrins to reduce foaming in latex paints. The latex paint formulation used in this Example is paint formulation #4 (Table 18).

Table 18
Paint Formulation #4

<u>Material</u>	<u>Kg</u>	<u>(Pounds)</u>
Methyl Carbitol	17.69	(39.0)
Acrylic latex, Rhoplex HG-74 (42.5%)	271.48	(598.5)
Texanol	16.78	(37.0)
Dowicil 75 premix	0.45	(1.0)
Water	2.27	(5.0)
Ammonium hydroxide (28%)	0.91	(2.0)
Water	18.14	(40.0)
Defoamer, Foamaster AP	1.91	(4.2)
Carbon Black, Harshaw W-7012	11.34	(25.0)
Acrylic Thickener, Acrysol RM-5 (30%)	10.34	(22.8)
Water premix	14.61	(32.2)
Ammonium hydroxide (28%)	0.99	(2.2)
Water	21.27	(46.9)

(Harshaw, which is a trademark of Harshaw, is Carbon black; and Dowicil 75, which is a trademark of Dow, is an antimicrobial agent.)

To test this formulation, the equivalent to 0 to 4.54kg (0 to 10 lbs) of ethoxylated beta-cyclodextrin per 378.51 (100 gallons) of paint was added to the paint. After equilibration overnight, the paints were applied to a seal Leneta 12-H-BW chart using a 7.62 cm, 0.95 cm (3", 3/8") nap synthetic fiber roller. The paint films were allowed to dry under ambient conditions. Surface defects in the film were rated by determining the frequency of defect on a 2 cm square area. The results are shown in Table 19.

Table 19
Surface Defects - Roller Foam Test
Addition of beta-cyclodextrin ethoxylated

<u>Additive Level</u>		<u>Foaming</u> <u>(Surface Defects / 2 cm sq.)</u>
<u>CD-ethoxylate</u>	<u>(lbs/100gal)</u>	
<u>kg/l</u>		
-----	-----	-----
0	(0)	5
1.19x10 ³	(1)	2
3.57x10 ³	(3)	1
5.95x10 ³	(5)	0
11.9x10 ³	(10)	0

The results in Table 19 show that at levels of 5.95x10⁻³ kg/l (5 lbs/100 gallons) of the ethoxylated cyclodextrin and higher, foaming defects are eliminated.

Claims

1. An aqueous system comprising a hydrophobic thickener characterised in that the aqueous system further

comprises a cyclodextrin.

2. An aqueous system according to claim 1, wherein the cyclodextrin is alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin, ethoxylated cyclodextrin or propoxylated cyclodextrin, preferably hydroxyethylcyclodextrin or hydroxypropyl-cyclodextrin.
3. An aqueous system according to claim 1 or claim 2 wherein if the cyclodextrin is unmodified the cyclodextrin is from about 0.5% to 2% by weight of the system and wherein if the cyclodextrin is modified the cyclodextrin is from about 0.5% to 10% by weight of the system.
4. An aqueous system according to any one of claims 1 to 3 wherein the system further comprises a complexing agent for complexing or desorbing the cyclodextrin from the hydrophobic thickener.
5. An aqueous system according to claim 4 wherein the complexing agent is an anionic surfactant, nonionic surfactant or a cationic surfactant.
6. An aqueous system according to claim 4 or claim 5 wherein the cyclodextrin and the complexing agent are present in approximately equimolar amounts.
7. An aqueous system according to any one of claims 1 to 6 wherein the hydrophobic thickener is a polyurethane.
8. An aqueous system according to any one of claims 1 to 7 wherein the aqueous system is a paint.
9. A thickener for preparing an aqueous system, the thickener comprising a cyclodextrin complexed with a hydrophobic thickener.
10. The use of a cyclodextrin for the preparation of an aqueous system comprising a hydrophobic thickener.
11. The use of a cyclodextrin in an aqueous system comprising a hydrophobic thickener for complexing with the hydrophobic thickener to reduce the viscosity of the system.
12. The use according to claim 10 or claim 11 wherein the aqueous system is a system according to any one of claims 1 to 8.
13. A process for preparing an aqueous system comprising mixing a hydrophobic thickener with a cyclodextrin, and optionally subsequently adding to the aqueous system a complexing agent for complexing or desorbing the cyclodextrin from the hydrophobic thickener.
14. A process according to claim 13 wherein the cyclodextrin is a cyclodextrin as defined in claim 2.
15. A paint comprising a cyclodextrin.

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